

(19) Japanese Patent Office (JP)

(12) Journal of patents open to the public (A)

(11) Number of the patent application: Open Patent 1986-4232

(43) Date of opening to the public: 10-1-1986

(51) Int.Cl.⁴
H 01 L 21/304

Identification number **Number for use inside the office**
D-7131-5F

**Patent examination claim Not yet claimed 1 invention
(in total 2 pages)**

(54) Title of the invention: Cleaning method of semiconductor substrate

(21) Number of application: Special application 1984-125760

(22) Date of application: 19-6-1984

(72) Inventor: TANNO Yukinobu
Inside Nippon Denki KK
5-33-1, Shiba, Minato-ku, Tokyo

(72) Inventor: TSUJI Mikio
Inside Nippon Denki KK
5-33-1, Shiba, Minato-ku, Tokyo

(71) Applicant for the patent: Nippon Denki KK
5-33-1, Shiba, Minato-ku, Tokyo

(74) Representative: Attorney KANNO Chu

DESCRIPTION

1. Title of the invention

Cleaning method of semiconductor substrate

2. Scope of the patent claim

(1) A cleaning method of semiconductor substrate with the characteristic of treating semiconductor substrate by dipping it in to a solution of an organic acid which is made to bubble with ozon/oxygen.

3. Detailed explanation of the invention

(technical field)

This invention is related to cleaning methods of semiconductor substrate.

(the former technique and its problems)

In the manufacturing of LSI the process of cleaning wafers in between each process necessitates a large number of treatments to remove dirt and filth and is an important technique for the improvement of the product. Important liquids used in this cleaning process are broadly divided into alkaline types and acid types. Widely known cleaning solutions are aqueous ammonia - hydrogen peroxide or hydrochloric acid - hydrogen peroxide (usually also referred to as RCA cleaning). Furthermore, mixed acid solutions are used such as sulfuric acid - hydrogen peroxide, sulfuric acid - nitric acid etc. The liquid is heated to a temperature of 60 - 150 °C and sometimes ultrasonic waves are jointly applied.

However, in the case of aqueous ammonia - hydrogen peroxide or hydrochloric acid - hydrogen peroxide, because of the fact that hydrogen peroxide immediately dissolves into H_2O and O in its developmental stage, their oxidation capacity deteriorates, their cleaning capacity cannot be maintained and it becomes necessary to intermittently supply hydrogen peroxide, thus complicating the industrial process. There are problems of processing sulfuric acid - hydrogen peroxide or sulfuric acid - nitric acid etc. as waste fluid. The disadvantages in the case of dissolving sulfuric acid, are that when it is reacted with water and heated to a temperature of more than 100 °C, there are safety problems and a large quantity of water is needed; in the case of nitric acid, nitric oxides etc. are generated, which fall under environmental pollution regulations etc., and it cannot be used in large quantities. In other words, the process costs become high.

Furthermore, instead of the above-mentioned acid - hydrogen

peroxide method, there is a widely known process method mentioned in Patent 1977-012063, which removes the resist membrane of semiconductor substrate. This method makes use of sulfuric acid and replaces the hydrogen peroxide with ozon, but in this method large amounts of water (- 10 times diluted) were needed for processing waste fluid of sulfuric acid etc. and it had safety and cost problems.

(Purpose of the invention)

This invention provides a treatment method to increase the safety, and moreover, to make it possible to perform a cheap process.

(Composition of the invention)

This invention is a cleaning method of semiconductor substrate with the characteristic of removing dirt from the surface of silicon wafers, by bubbling ozon/oxygen in a tank which contains an organic acid as cleaning solution.

(Principles and effect of the invention)

Amongst the organic acids formic acid is a strong acid which can be reduced (deoxidized). On the other hand, acetic acid is a weak acid. By reacting them respectively with heavy metals (M) and substituting the H of the -COOH radical, a heavy metal consisting of -COOM is made.

Moreover, by making ozon bubble, organic waste matter is oxidized by means of the ozon, and can be dissolved and removed.

In other words, this invention performs cleaning by means of heavy metals on the semiconductor substrate (wafer) surface which form formate or acetate and by dissolving the organic waste matter by means of ozon.

(Operation example)

Next, an explanation will be given of a comparison between this invention and the former example. Hereafter, this invention will be explained following an operation example. In this invention cleaning takes place as follows: an organic acid (for example formic acid, acetic acid) is poured into a cleaning tank, heated to 100 - 150 °C, semiconductor substrate is dipped into this liquid, ozon/oxygen is made to bubble from the bottom of the tank and the said substrate is treated.

As cleaning tank a product made of teflon was used in this invention, the temperature of the liquid was increased and kept under control by means of a quartz heater. Furthermore, ozon/oxygen was made to bubble from the bottom of the tank by means of a Pyrex gas distributor. Using a similar type of tank, cleaning was performed with the RCA liquid of the former invention $\text{NH}_4 \text{ OH} - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ (1:1:5) at a liquid temperature of 80 °C during 10 minutes.

Next, according to the method of this invention, the same tank as mentioned above and wafers of an identical lot were used and these wafers were dipped into a solution of formic or acetic acid. This time the solution was heated to a temperature of 100 - 150 °C. Next, ozon/oxygen was made to bubble from the bottom of the tank and cleaning was performed during 10 minutes.

The wafers cleaned with the $\text{NH}_4 \text{ OH} - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ solution of the former method and the wafers cleaned with the formic acid - ozon - O_2 solution of this method were submitted to a steam process (at 950 °C during 10 minutes in a $\text{H}_2 - \text{O}_2$ atmosphere); the lifetime was measured by means of a non-contact process, and the V_{FB} (flat band voltage) was evaluated by means of a MOS C-V method, the results of which are shown in table 1.

Table 1

Cleaning method	Lifetime (μsec)	V_{FB} (V)
Former method ($\text{NH}_4 \text{ OH}$ type)	7	- 0.9
Method of this invention (ozon/formic acid)	20	- 1.0

(Efficacy of this invention)

As shown in table 1, the cleaning method of this invention has a re-coupling lifetime value which is three times higher compared to that of the former RCA solution, which demonstrates that its cleaning effect is superior. On the other hand, the V_{FB} (flat band voltage) found by means of the MOS - CV method does not differ greatly from the former method. It was - 1.0.

As shown above, the cleaning method of this invention compared to the cleaning effects of the former method, is more than equal, and its goal has been fully achieved.

Furthermore, this invention gives little rise to problems such as heat generation by reacting sulfuric or nitric acid with water, or problems of environmental pollution. This is because formic and acetic acid at high temperatures (~ 150 °C) easily dissolve into CO , CO_2 , H_2O etc. and dissolution is further accelerated by means of ozon. Therefore, at the time of the waste fluid process this invention has the effect of easily dissolving, also in water, and it not only enables rational industrial operation without safety problems, but also enables to lower the costs necessary for the process.

Applicant for the patent:
Representative:

Nippon Denki KK
Attorney KANNO Chu(seal)